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Abstract

A study is performed to elucidate the chemical kinetic mechanism of combustion of toluene. A detailed chemical kinetic mechanism for toluene was improved by adding a more accurate description of the phenyl + O_2 reaction channels. Results of the chemical kinetic mechanism are compared with experimental data obtained from premixed and nonpremixed systems. Under premixed conditions, predicted ignition delay times are compared with new experimental data obtained in shock tube. Also, calculated species concentration histories are compared to experimental flow reactor data from the literature.

Critical conditions of extinction and ignition were measured in strained laminar flows under nonpremixed conditions in the counterflow configuration. Numerical calculations are performed using the chemical kinetic mechanism at conditions corresponding to those in the experiments. Critical conditions of extinction and ignition are predicted and compared with the experimental data. For both premixed and nonpremixed systems, sensitivity analysis was used to identify the reaction rate constants that control the overall rate of oxidation in each of the systems considered.

Introduction

Alkylated benzenes are an important class of hydrocarbons because they comprise a significant portion of gasoline and diesel fuels. Knowledge of the oxidation chemistry of alkylated benzenes is needed in developing predictive models that can treat autoignition, and premixed and non-premixed burning of transportation fuels in internal combustion engines. Toluene has one of the simplest molecular structures of the alkylated benzenes and is a reasonable starting point for the development of detailed chemical kinetic reaction mechanisms for alkylated benzenes. Much previous work has been done on the oxidation of toluene. Several research groups have developed detailed chemical kinetic reaction mechanisms for toluene. Most recently, Klotz et al. [1] supplemented the toluene mechanism of Emdee et al. [2] to improve the predictions for the intermediates 1,3 butadiene, acetylene and benzaldehyde. Zhong and Bozzelli [3-5] developed a more accurate description of radical additions to cyclopentadiene and associations with

cyclopentadienyl radical; they included these reactions in a detailed chemical kinetic mechanism for toluene that they developed. Lindstedt and Maurice [6] developed a very comprehensive toluene mechanism whose predictions they compared to experimental results from counterflow diffusion flames, plug flow reactors, shock tubes and premixed flames. Emdee et al. [2] developed a detailed chemical kinetic mechanism for toluene that was benchmark for many years. There are quite a few experimental studies of toluene oxidation whose data are very useful for mechanism validation. Several experimental studies of toluene oxidation in a flow reactor were performed at Princeton University [1,2,7,8]. Ignition of toluene in a rapid compression machine was preformed by Griffiths et al. [9] and by Minetti et al. [10]. Their rapid compression machine results show that toluene oxidation chemistry lacks the two stage ignition observed in paraffin fuels. The present work offers new results for shock tube ignition of toluene and new results for ignition and extinction under non-premixed conditions. These experiments provide additional data for validating chemical kinetic mechanisms for toluene.

Experimental

Shock Tube experiments
The experiments were performed in a stainless steel 7.8 cm diameter shock tube at DCPR-CNRS-NANCY. The reaction and driver parts were separated by two terphane diaphragms, which were ruptured by suddenly decreasing the pressure in the space separating them. The driver gas was helium and the reacting mixture was diluted in argon. The incident and reflected shock velocities were measured by four piezo-electric pressure transducers located along the reaction section. The state of the test gas behind the incident and the reflected shock waves was derived from the value of the incident shock velocity by using classical, one-dimensional, shock equations of mass, momentum, and energy conservation applied to an ideal gas.

The pressure profile displayed three rises, which were due to the incident shock wave, the reflected shock wave and the ignition, respectively. The onset of ignition was, however, most accurately detected by OH radical emission at 306 nm through a quartz window with a photomultiplier fitted with a monochromator at the end of the reaction part. The last pressure transducer was located at the same place along the axis of the tube as the quartz window. The ignition delay time was defined as the time interval between the pressure rise measured by the last pressure transducer due to the arrival of the reflected shock wave and the rise of the optical signal by the photomultiplier up to 10% of its maximum value.

Oxygen, argon and helium were purchased from Air Liquide-Alphagaz and toluene was provided by Aldrich (purity : 99.8 %). The toluene concentration in the reactants was kept constant at 1.25 percent. The equivalence ratios examined were 0.5, 1.0 and 1.5. The reflected shock pressures and temperatures ranged from 8.0 to 9.4 atm and 1300 to 1900 K, respectively.

Extinction and Ignition under Non-Premixed Conditions

Figure 1 shows a schematic illustration of the counterflow burner. A detailed description of this burner and the experimental procedure are given elsewhere [11]. A jet of prevaporized fuel mixed with nitrogen is introduced from the bottom duct and a jet of air from the top duct [Fig. 1]. The jet of air is heated in the ignition experiments, but not in the extinction experiments. Several fine wire screens are placed near the exit of the fuel and oxidizer ducts to make the exit velocity profile nearly uniform. An annular "curtain" flow of nitrogen flows parallel to and surrounds the fuel stream and oxidizer stream, respectively. During the experiments, the momenta of the counter-flow reactant streams are equal. All gaseous flows are measured by computer-regulated mass flow controllers. The temperature of the air at the exit of the air duct is measured with a Pt-Pt 13% Rh thermocouple. The accuracy of the radiation-corrected temperatures is expected to be +/- 25K. The experiments were carried out at atmospheric pressure.

Detailed Chemical Kinetic Mechanism.

The detailed chemical kinetic mechanism for toluene was assembled by adding the toluene and benzene reaction mechanism of Zhong et al [2-5] to the C1-C4 mechanism of Curran et al. [12]. The ultimate objective of this work is to add toluene as a fuel component to detailed chemical kinetic mechanisms for alkanes that have been developed at LLNL [13]. This combined alkane-toluene mechanism will provide a more complete mechanism for simulating gasoline or diesel fuels.

The toluene mechanism was improved in several ways. The reaction rate constants for phenyl + O_2 system developed by Bozzelli et al. [15] were incorporated. These reaction channels included new products for which consumption reactions were added. The phenyl + O_2 rate constants were found to play an important role under shock tube conditions. The reaction of benzyl with O atoms was added:

$$C_6H_5CH_2. + O \leftrightarrow C_6H_5CHO + H \quad .$$
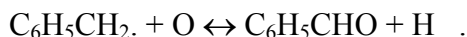
The rate constant was taken from Baulch et al. [15], k= 3.3 x 10^{14} cm^3/(mol-s). The inclusion of the reaction was essential for modeling the shock tube experiments. Its prior omission was identified by comparing the computed results of the current mechanism with that of Da Costa et al. [16]. The rate constant for the initiation reaction (toluene + O_2 => benzyl + HO_2) was updated using one half the rate constant of allylic isobutene + O_2 [17] (k=9.3 x 10^8 T$^{1.301}$ exp(-40939.0 cal/RT) cm^3/(mol-s)). Our estimate is 50 percent higher than the estimate of Walker [18] at 1000 K. This reaction rate constant controls the induction period under flow reactor conditions. Reactions to consume bicyclopentadiene were also added.

Shock Tube Comparisons

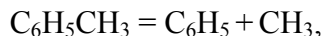The ignition in the shock tube was simulated using the Senkin code [19] assuming constant volume combustion after the reflected shock passes through the mixture. The predicted results were compared to measured results in Fig. 2. The computed ignition delay was calculated using the inflection in the temperature profile as an indication of ignition. The 10 percent of the maximum in the OH concentration gave almost identical

results over the temperature range considered. We did not attempt to simulate OH emission. In general, the predicted ignition delays are too long compared to the experimental delays, particularly at higher temperatures.
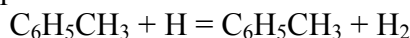
Standard Senkin sensitivity analysis [19] was performed to determine the reaction rate constants that control the oxidation of toluene under shock tube conditions. The Senkin code gives the change in species concentration for an incremental change in reaction rate constant. The toluene species concentration was chosen as an indicator of the overall reactivity of the system. An alternate choice of OH species concentration produced similar results. The sensitivity of the toluene concentration at 6 μs to a change in reaction rate constant is shown in Fig. 6. At 6 μs, the initial toluene is about 50 percent consumed. Positive sensitivities indicate an increase in rate constant increases the toluene concentration and retards the overall rate of reaction, while negative sensitivities indicate an increase in rate constant decreases the toluene concentration and increases the overall rate of reaction. Only a few reactions control the toluene concentration and overall reactivity at 1750 K [Fig. 3]. (1750 K was chosen because the predicted and measured ignition delays had the largest discrepancy at the highest temperature). The controlling reactions are the toluene decomposition reactions and $H + O_2$ chain branching. For the toluene decomposition channel,
$$C_6H_5CH_3 = C_6H_5CH_3 + H,$$
the rate of Baulch et al. [15] was used ($k = 6.31 \times 10^{15} \exp(90.3 \text{ kcal/RT}) \text{ s}^{-1}$) which is 30% lower at 1700K than the high pressure estimate of Hippler et al. [22]. For the other decomposition channel,
$$C_6H_5CH_3 = C_6H_5 + CH_3,$$
the rate constant was chosen to be analogous to $C_3H_6 = C_2H_3 + CH_3$ ($k = 7.94 \times 10^{16} \exp(-104.0/RT) \text{ s}^{-1}$) from [4].) This rate constant is less well known than the rate constant for the H atom product channel. The abstraction reaction
$$C_6H_5CH_3 + H = C_6H_5CH_3 + H_2$$
exhibits a high sensitivity. We used the rate constant from Baulch et al. [15]. This rate constant has an uncertainty of about a factor of 2 at 1700K. Overall, the disagreement between the model and the experiment shock tube results could be explained by uncertainties in these rate constants. This possibility will be explored in future work.

Flow Reactor Comparisons

The flow reactor was simulated using the Senkin code [19]. The predicted results are compared to the measurements of Klotz et al. [1] in Figs. 4 and 5. The results for the fuel profile look reasonable, but improvements need to be made in the predictions for many of the intermediate species concentrations. This is due to the new products resulting from the phenyl + O_2 reaction discussed above. We need to work at detailed pathways for the ring opening intermediates from unimolecular dissociation of the phenylperoxy radical.

Senkin sensitivity analysis [19] was performed to determine the reaction rate constants that control the oxidation of toluene under flow reactor conditions. The toluene concentration was chosen as an indicator of the overall reactivity of the system. The

sensitivity of the toluene concentration at 100 ms to a change in reaction rate constant is shown in Fig. 6. At 100 ms, the initial toluene is about 60 percent consumed. Negative sensitivities indicate that the reaction accelerates the overall rate of reaction and positive sensitivities indicate the opposite effect. The reaction exhibiting the highest sensitivity is

$$C_6H_5CH_3 + O_2 = C_6H_5CH_2. + HO_2$$
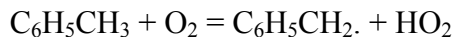
which is the reaction that initiates the radical production in the flow reactor and controls the duration of the induction period. The same sensitivity result was found by Emdee et. al. [2]. The detailed chemical kinetic model probably does not simulate well the initiation phase in the flow reactor. Senkin assumes the reactants are mixed at a molecular scale at time zero and the reactants instantaneously reach the initial temperature in the reactor. In the actual flow reactor device, mixing of the fuel, nitrogen and oxygen streams occur in a finite time on the order of 1 msec and there is uncertainty in the residence time in the diverging section of the inlet to the flow reactor. Traditionally, the inability of the model to simulate the initial mixing and entry flow has justified shifting of the computed concentration histories relative to the measured histories. Since the present model does not treat the details of the entrance section of the flow reactor, comparisons of the modeling and experimental results do not give any information about initiation of toluene reaction or specifically, the rate constant of the above initiation reaction. We have not changed our original estimate of this rate constant.

The second most sensitive reaction is the reaction of benzyl and O_2:

$$C_6H_5CH_2. + O_2 = C_6H_5O. + CH_2O$$
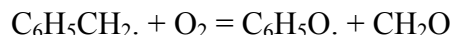
The rate constant of this reaction, k = 5.30x 10^{13} $T^{-1.07}$ exp(-10840 cal/RT), was taken from Zhong and Bozzelli [4]. This reaction occurs through at 4-membered transition state where the terminal oxygen on the benzyl peroxy radical adds to the benzene ring. The third most sensitive reaction is the familiar $H + O_2$ chain branching reaction. The fourth most sensitive reaction show a positive sensitivity because it removes H atoms that would otherwise lead to change branching via $H + O_2$. The ninth reaction promotes toluene oxidation by producing an OH radical:
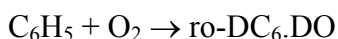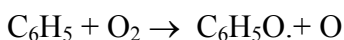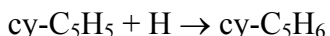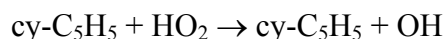
$$C_6H_5CH_2. + HO_2 = C_6H_5CH_2O. + OH$$
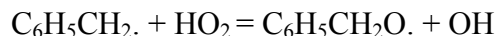
HO_2 radicals that feed this reaction are produced by $HCO + O_2 = CO + HO_2$ which is partially why this sixth most sensitive reaction is promoting.

Comparisons with Strained Laminar Flow under Non-Premixed Conditions

The detailed chemical kinetic mechanism was tested by comparing computed results with experiments performed under strained, non-premixed conditions. Extinction and ignition in counterflow flames were computed with the FlameMaster code [20]. Solutions could not be obtained with the 379 species detailed chemical kinetic mechanism due to numerical "stiffness" problems. The detailed chemical kinetic mechanism was reduced using the NIST XSenkplot. [21]. Reduced mechanisms were obtained under shock tube conditions and flow reactor conditions and combined to yield a 45 species mechanism. Any reaction in the detailed mechanism that involved only these 45 species was retained

in the reduced mechanism. The comparison of the computed and measured ignition and extinction results is shown in Figs. 7 and 8. Under ignition conditions, the experiments indicate a lower ignition temperature at a given strain rate than the model. Under extinction conditions, the experiments indicate that toluene/air tolerates a higher rate of strain at extinction than the predictions. Thus in both types of experiments, the model predicts that toluene/air is overall less reactive than observed in the experiments. This result is consistent with comparisons between the model predictions and experimental results from the shock tube above 1400K. (No conclusion about the ability of the model to predict ignition (or extinction) can be drawn from the flow reactor comparisons because of the problem of not properly treating the details of the initial mixing and entrance section of the flow reactor.)

The sensitivity results for ignition under non-premixed conditions are given in Fig. 9. The analysis performed by FlameMaster [20] gives the change in maximum OH concentration for an incremental change in rate constant as indicated in Fig. 9. Flamemaster considers forward and reverse rate constants as separate parameters for the purposes of sensitivity analysis.   The analysis was performed for a reactive flow solution very near ignition. Positive sensitivities indicate an increase in rate constant increases the OH concentration and accelerates the overall rate of reaction, while negative sensitivities indicate an increase in rate constant decreases the OH concentration and retards the overall rate of reaction. The $H + O_2$ chain branching and reactions of toluene with O_2 and OH give very high sensitivities as under flow reactor conditions. The reactions that give high sensitivity in non-premixed conditions but not in the flow reactor or shock tube conditions are reactions that involve the cyclopentadienyl radical and the phenyl $+ O_2$ reaction:

$$cy\text{-}C_5H_5 + HO_2 \rightarrow cy\text{-}C_5H_5 + OH$$

$$cy\text{-}C_5H_5 + H \rightarrow cy\text{-}C_5H_6$$

$$C_6H_5 + O_2 \rightarrow C_6H_5O. + O$$

$$C_6H_5 + O_2 \rightarrow ro\text{-}DC_6.DO$$

where $ro\text{-}DC_6.DO$ is O=CC=CC=CC.=O   An important uncertainty in the phenyl $+ O_2$ system is the branching ratio between the two product channels given above. The O-atom product channel is accelerating and the other ring-opening product channel is retarding [Fig.9]. The branching ratio depends on the relative barrier heights for phenylperoxy going to O-O bond breakage versus to ring opening [14].

Conclusions

The detailed chemical kinetic model for toluene was improved by adding a more accurate description of the phenyl $+ O_2$ reactions.   New data obtained under non-premixed conditions in a counterflow configuration and obtained in a shock tube were compared to results of the detailed chemical kinetic model. Sensitivity analysis was used to identify reactions whose rate constants control the overall rate of oxidation. This information can be used to obtain future improvements of the agreement between the model and experiments. The reactions that exhibited high sensitivity included toluene

decomposition reactions and toluene reaction with O_2. Also, reactions with the cyclopentadienyl radical and the phenyl + O_2 reactions were shown to be important.

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Figure captions

Fig. 1. Schematic of apparatus for experiments on autoignition.

Fig. 2. Predicted and measured ignition delay times under shock tube conditions. (T = reflected shock temperature).

Fig. 3. Sensitivity of the toluene concentration to changes in individual rate constants under shock tube conditions (ϕ=1.0, reflected shock temperature =1750 K)

Fig. 4. Predicted and measured concentration histories under flow reactor conditions. (ϕ=0.76, $N_2 \cong 98\%$, initial temperature=1173 K, atmospheric pressure, time is residence time in flow reactor).

Fig. 5. Predicted and measured concentration histories under flow reactor conditions. (ϕ=0.76, $N_2 \cong 98\%$, initial temperature=1173, atmospheric pressure, time is residence time in flow reactor).

Fig. 6. Sensitivity of the toluene concentration to changes in individual rate constants under flow reactor conditions (ϕ=0.76, $N_2 \cong 98\%$, initial temperature=1173 K, atmospheric pressure, residence time = 100 ms)

Fig. 7. Ignition of toluene in a non-premixed counterflow stream.

Fig. 8. Extinction of toluene in a non-premixed counterflow diffusion flame.

Fig. 9. Sensitivity of the OH radical concentration to changes in individual rate constants under non-premixed ignition conditions near ignition (strain rate = 400 s^{-1}, oxidizer temperature = 1343 K).
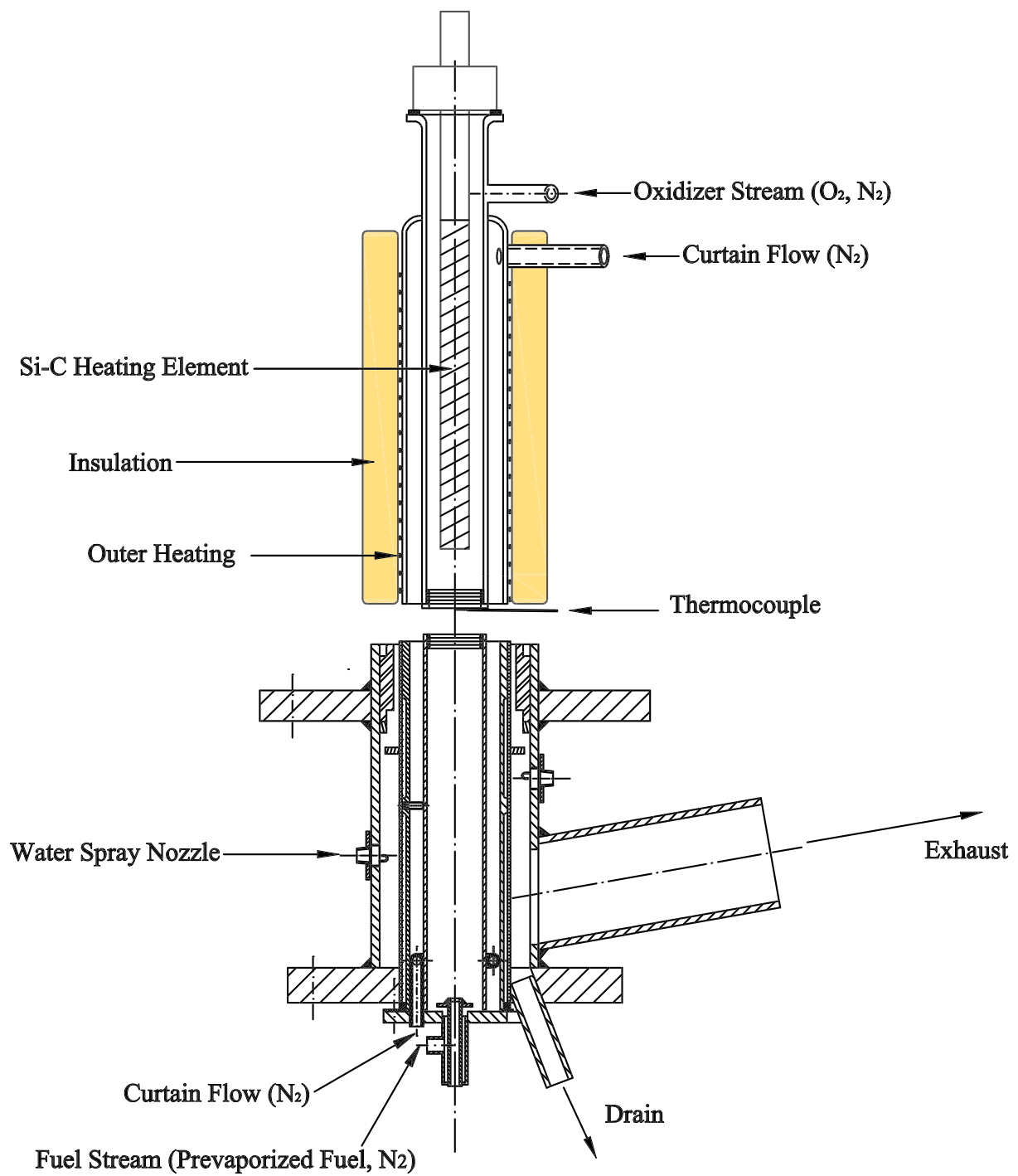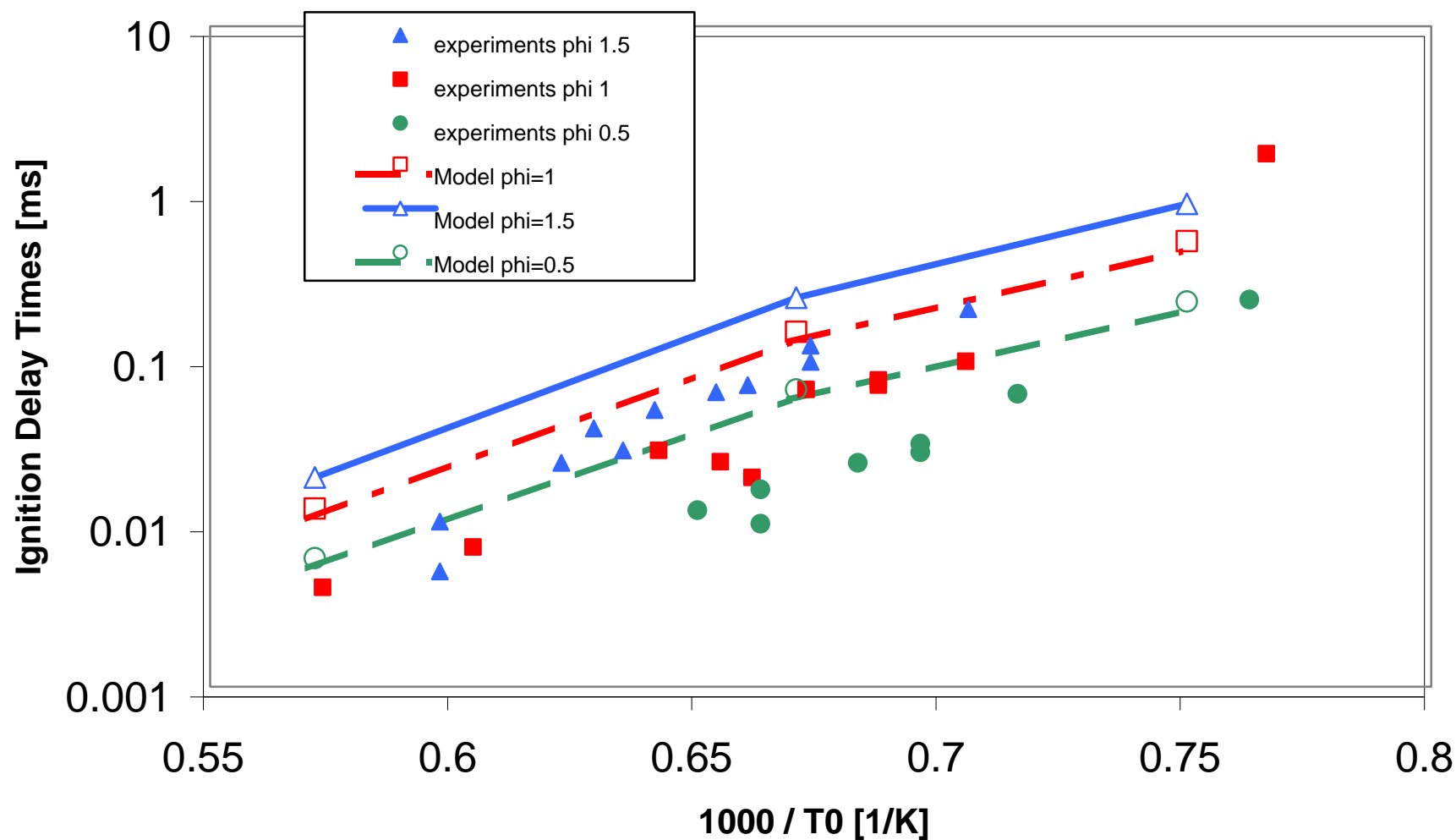
Figure 1: Schematic illustration of the apparatus used for experiments on autoignition.

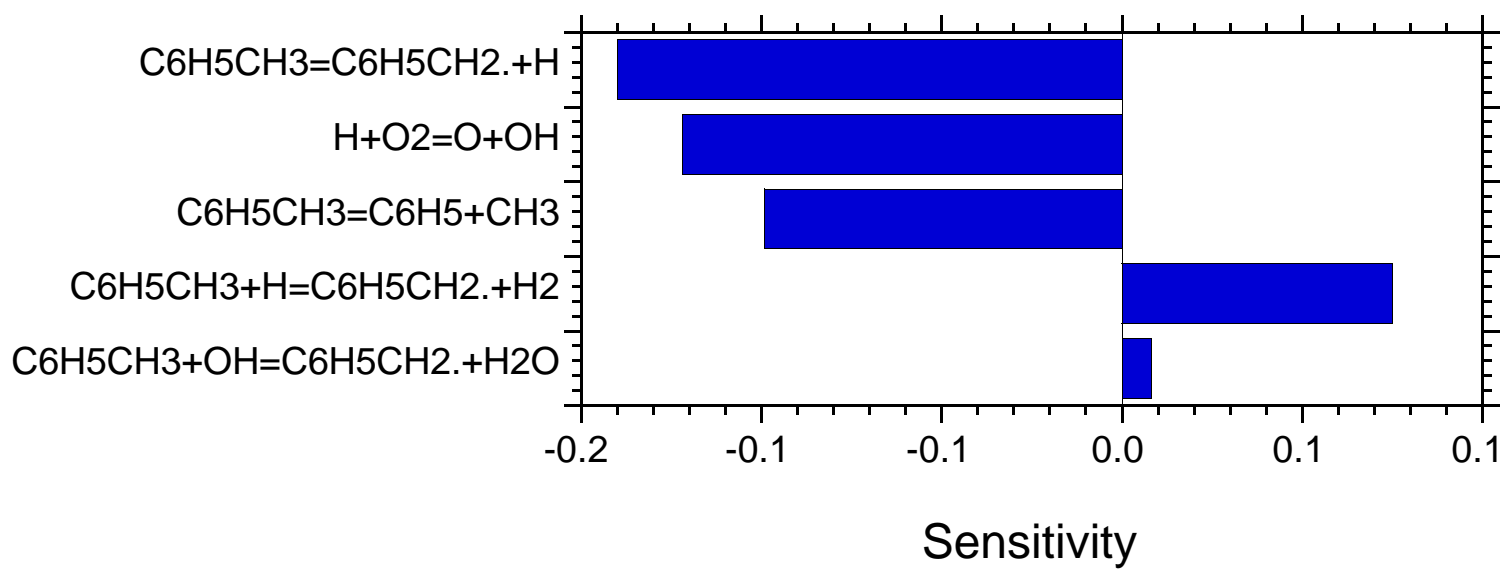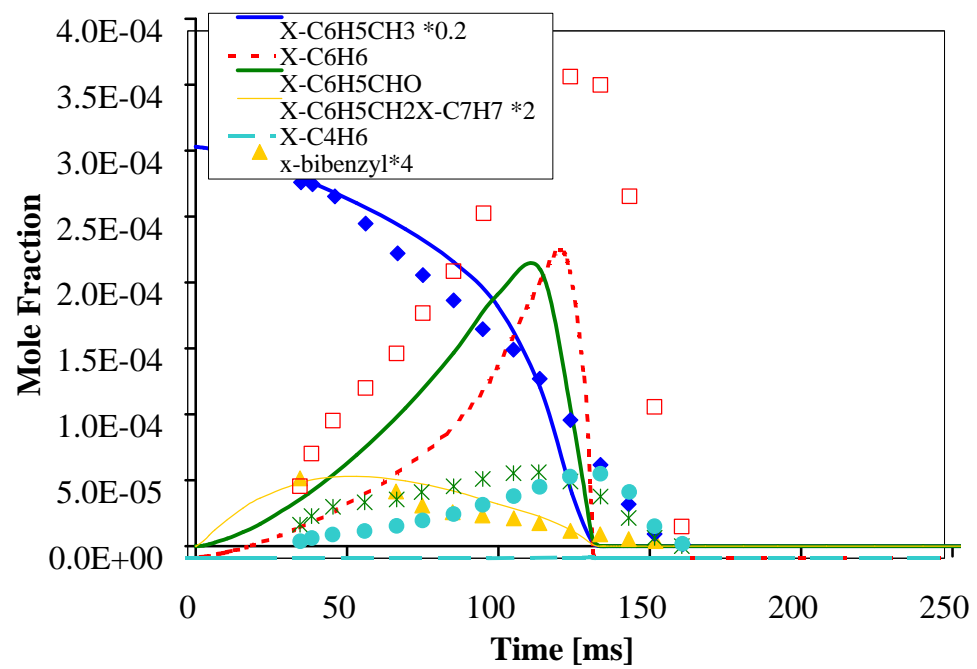Fig. 2: Shock Tube Ignition of Toluene/O₂/Ar Mixtures
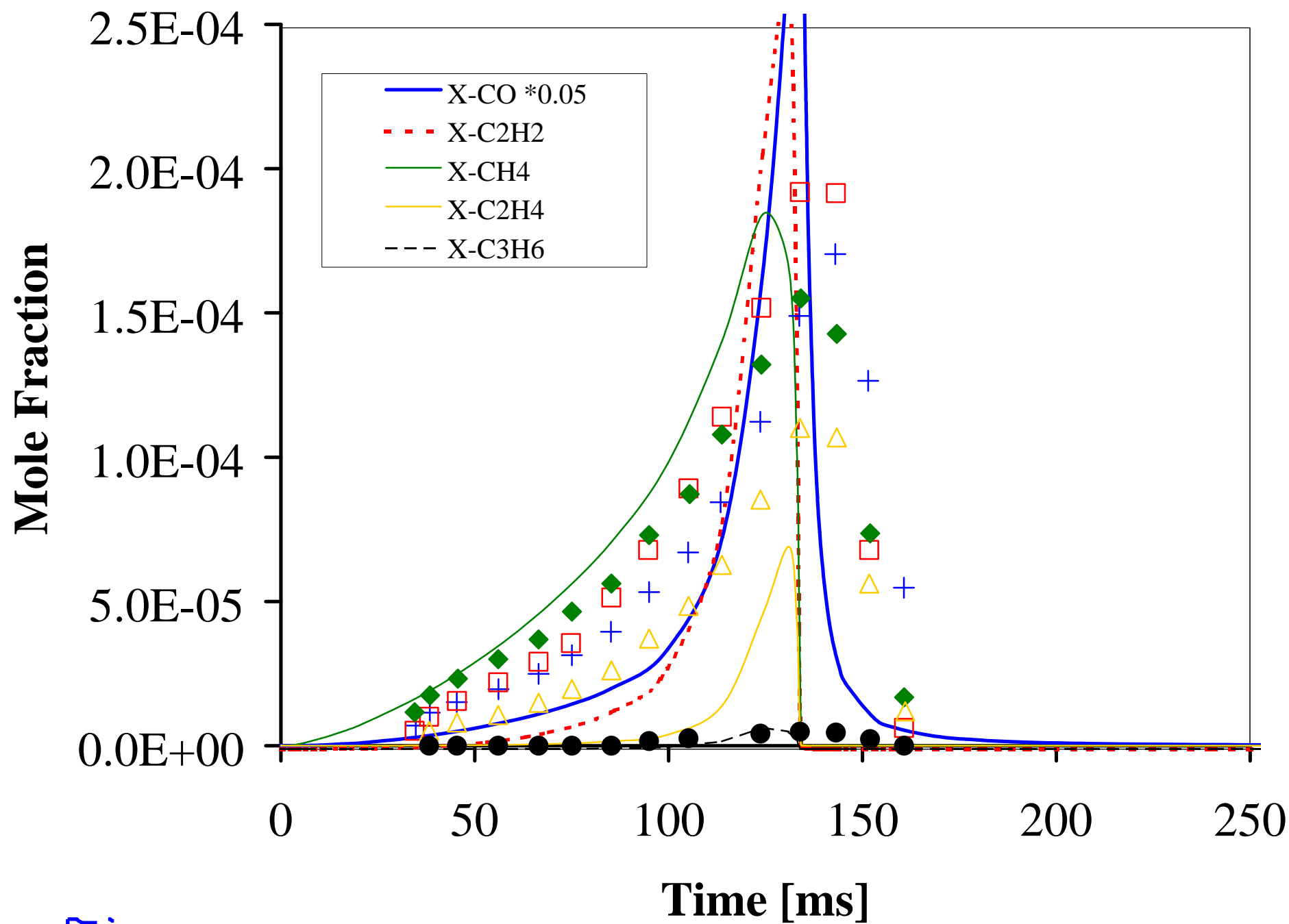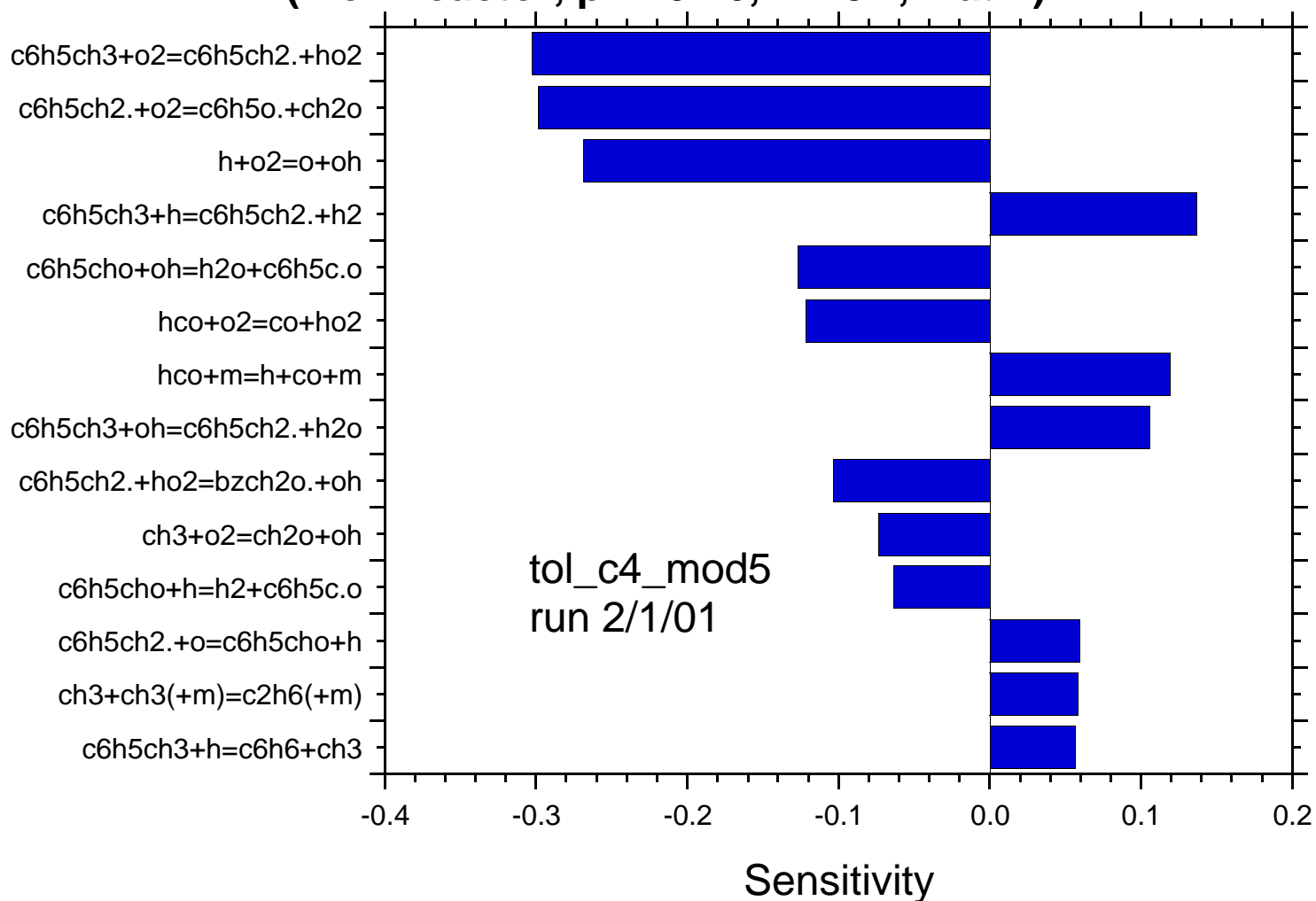
Fig. 3

Fig 4.
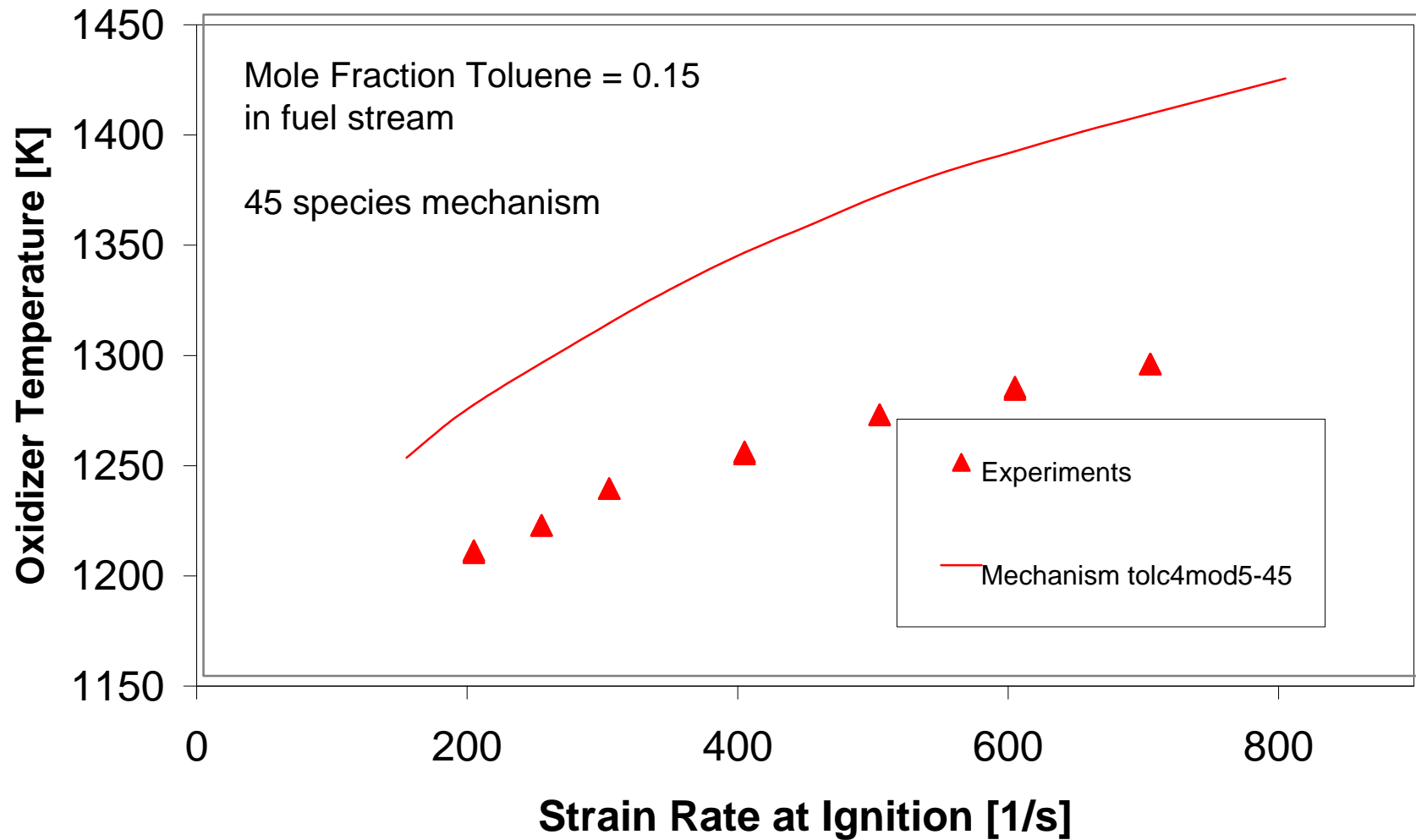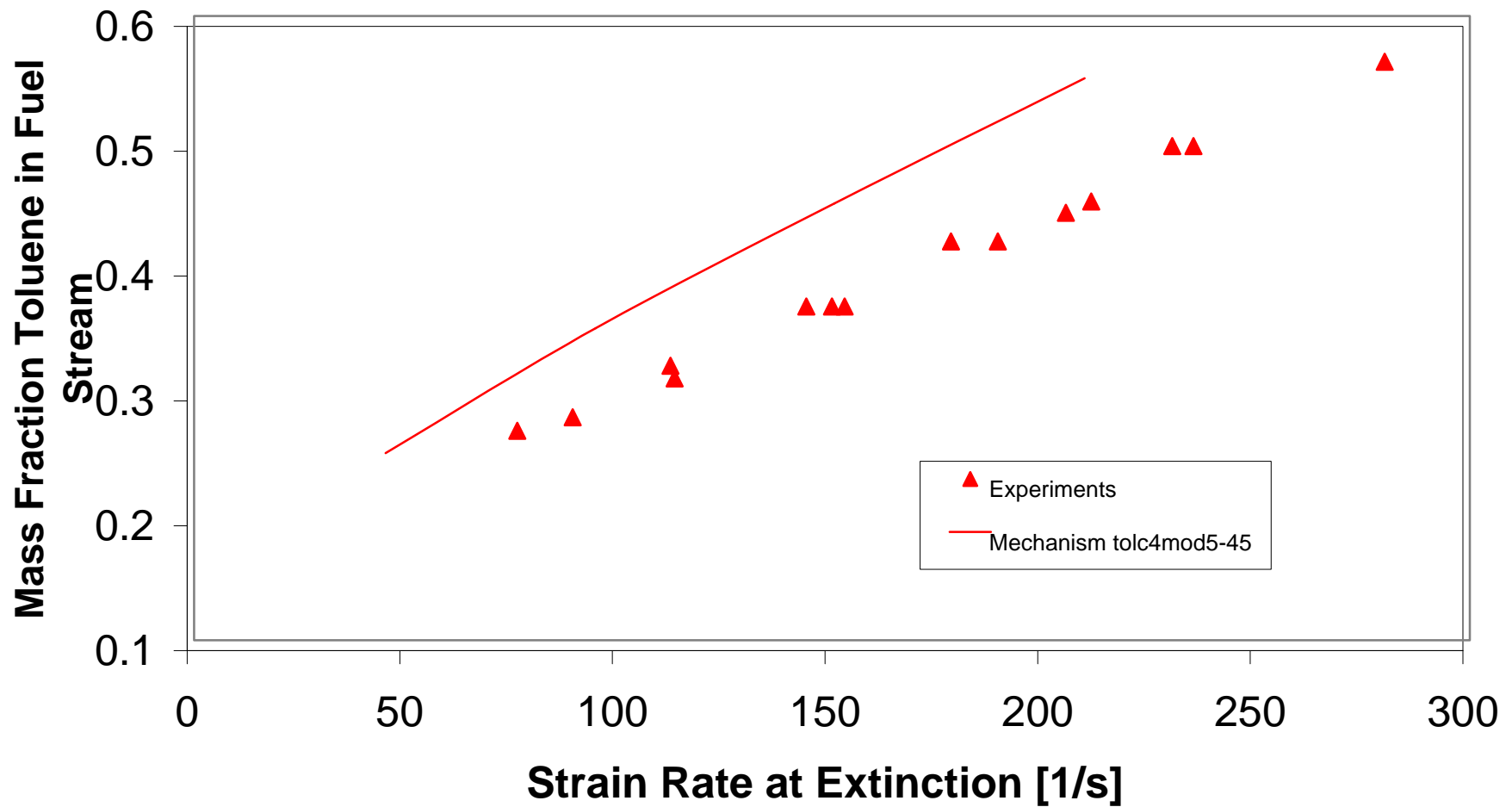
Fig. 5

Fig. 6

Effect of Rate Constants on Toluene Concentration at 100 ms (Flow reactor, phi=0.76, 1173K, 1 atm)

Ignition of Toluene in a Non-premixed Counterflow Stream

Mole Fraction Toluene = 0.15
in fuel stream

45 species mechanism

▲ Experiments

— Mechanism tolc4mod5-45

Oxidizer Temperature [K] (y-axis: 1150, 1200, 1250, 1300, 1350, 1400, 1450)

Strain Rate at Ignition [1/s] (x-axis: 0, 200, 400, 600, 800)

Fig 7

Extinction of Toluene/Air in a Non-premixed Counterflow Diffusion Flame

Legend:
▲ Experiments
— Mechanism tolc4mod5-45

X-axis: Strain Rate at Extinction [1/s]
Y-axis: Mass Fraction Toluene in Fuel Stream

Fig 8.

Fig. 9